Reprinted from TEXTILE RESEARCH JOURNAL, Vol. 32, No. 7, July, 1962
Printed in U. S. A.

Soil Burial of Fabrics Treated with Minimal Concentrations of Fungicides

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Abstract

Strips of cotton duck were treated with low concentrations of fourteen commercial and experimental fungicides and subjected to a soil burial test. Comparative effectiveness of the compounds was determined in terms of dosage required to yield 50% loss in breaking strength (ED_{50}) at ten days burial.

The effectiveness of the several compounds used ranged from 0.01% to 1.5% based on concentration of the treating solution. The most commonly used compounds were all effective at 0.5% or less. The effective soil burial life was found to be a function of the concentration within the limits of time and concentration studied. Several compounds were investigated in factorial combinations at concentrations known to result in partial effectiveness at ten days when used singly. No significant synergism was observed. The significance of minimal concentrations in relation to the breakdown process is discussed.

Introduction

Although there is considerable information in the literature on the effectiveness of various fungicides applied to cotton fabric, these data are of little value in comparing the inherent effectiveness of the different compounds. This is mainly due to the lack of standard experimental conditions and adequate controls. Also, the concentrations employed were those recommended for actual use and were, therefore, relatively high. The work reported here was designed to provide a comparative measure of the minimal effective levels of a number of fungicides under conditions of the laboratory soil burial test.

Materials and Methods

The fabric used in this study was an 8.25-oz cotton duck, unsized and unbleached. It was cut into standard 1 × 6-in. strips as described in Method 5104 of Federal Specification CCC-T-191b [4].

The compounds used (Table III) were selected to represent a variety of textile fungicides. They were dissolved or suspended in organic solvents (principally acetone, methyl alcohol, and xylol) in graded concentration series.

The fabric strips were treated at room temperature by dipping them individually in the fungicide for a carefully timed 10-sec period, removing and draining for a carefully timed 5-sec period. The strips were held by two wire hooks, one at each end, and were folded so as to form a loop during the dipping and draining operation. At the end of the 5-sec drain the strip was momentarily touched to the side of the vessel holding the fungicide and immediately transferred to the drying rack. At this point the strips were thoroughly wet, but most of the excess liquid had drained off. The drying rack was adapted from a Patterson-Kelly Twin Shell Dry Blender [1] arranged with rods spaced so as to receive the wire hooks on the strips and hold the strip in a stretched position. The frame of the blender rotated at 33 rpm, and the strips were placed so as to rotate end over end around a circle about a foot in diameter. The rotation, while slow enough to set up negligible centrifugal force, served to nullify the effects of gravity. In this way the concentration gradient which would have occurred had the strips merely been hung up to dry was prevented. The time required to dry depended upon the solvent used and ranged from a few minutes for acetone to 10 or 20 min for less volatile solvents such as xylol.

To determine the variation in the amount deposited on the strips, two groups of 4 strips each treated with copper naphthenate were analyzed for copper by a rubeanic acid (colorimetric) method. The variation is shown in Table I. It can be seen that there is no recognizable tendency toward any gradient either across the strip or between ends and middle. The total pickup of the strips treated with the lower concentration had a mean of 0.28% (standard deviation = 0.017%); for the higher concentration the mean was 0.34% (standard deviation = 0.005%). The variability encountered was considered satisfactory since it was appreciably less than the differences between successive steps in the concentration series. This judgment was borne out by the appearance of strips removed from soil burial in a degraded condition at which time strips belonging to different concentrations could generally be separated on visual criteria alone.

The average wet pickup of the strips was found to be about 100%, hence the nominal concentration of the treating solution was taken as the amount deposited on the strip.

The strips were subjected to the standard soil burial and breaking strength tests as described in

[1] Patterson-Kelly Co., Inc., East Stroudsburg, Pa.

TABLE I. Variation in Deposition of Copper (as Copper Naphthenate) on Strips Treated at Two Concentrations

	Percent copper	
	Lower concentration	Higher concentration
Strips cut crosswise		
Ends	0.26, 0.28	0.33, 0.34
Middle	0.28, 0.29	0.34, 0.34
Strips cut lengthwise		
Sides	0.25, 0.26	0.34, 0.34
Middle	0.27, 0.31	0.34, 0.35

TABLE II. Breaking Strength (lb) of Strips Treated with 0.02% Zinc Dimethyldithiocarbamate on Four Successive Burial Periods

	Days in soil burial			
	6	7	8	9
	52	30	23	12
	68	38	27	10
	67	47	18	13
Mean, lb	62.3	38.3	22.7	11.7
% of control	73	45	27	14

Methods 5762 (except for the leach) and 5104 of Federal Specification CCC-T-191b [4].

Each determination was the average of 3 replicate strips, and each treatment was replicated at least 3 times. The use of 3 replicates in place of the usual 5, 10, or more was necessitated by the large number of different treatments in the study. It was found that this replication was adequate for the purpose. A typical set of data is given in Table II. These data correspond to one of the curves for 0.02% zinc dimethyldithiocarbamate shown in Figure 2.

Experimental

The rate of breakdown of untreated control strips is shown in Figure 1. This is a composite of soil activity controls of 15 replicate experiments, 3 strips each, for a total of 45 strips per point, except the point at zero time, which represents 89 strips. The standard deviation and the standard error of the mean is given for each point. The uniformity of the course of breakdown and the low variability between experiments is striking. It indicates that under carefully controlled conditions, the soil burial test is indeed a very reproducible measure of the degradation of fabric. The point at 50% breakdown occurs very close to three days burial.

In testing treated fabrics the solutions were first prepared in a wide range of concentrations. Narrower dilutions were then prepared to yield a half-life of 10 days, defined as that concentration of treating solution allowing 50% breakdown in 10 days' burial (ED_{50}). Ten days was chosen as a convenient end point, since it was appreciably greater than that needed by untreated controls yet not unreasonably long. Also, it was found that with very long incubations associated with high concentrations, three replicates did not result in smooth breakdown curves, although this number was obviously adequate in the lower ranges (Figure 2).

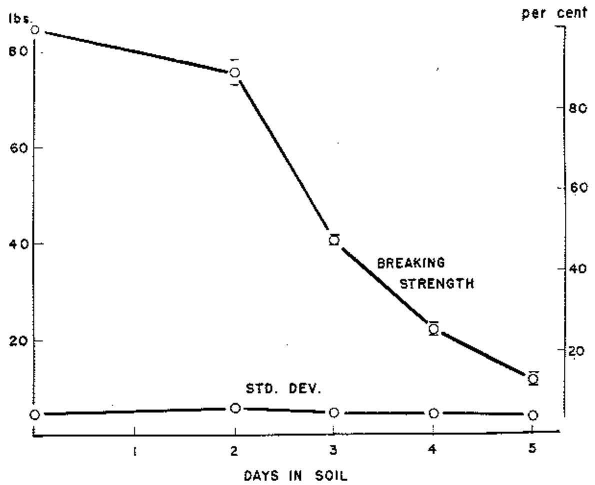

Fig. 1. Course of breakdown of untreated cotton duck control fabrics in soil burial. Data combined from 15 experiments, 3 strips per experiment. The point at 0 time is based on 89 breaks. Each point in the breakdown curve includes the standard error of the mean, indicated by short horizontal lines.

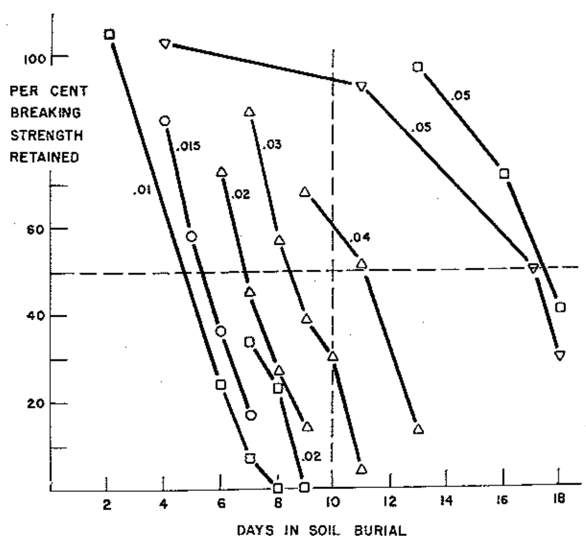

Fig. 2. Deterioration in soil burial of cotton duck treated with zinc dimethyldithiocarbamate. Results of four experiments are represented by different symbols. Concentrations of treating solution ranged from 0.01 to 0.05%. The crossed coordinates indicate the ED_{50} at 10 days.

The method of establishing the end point (ED_{50}) at 10 days is illustrated by results with duck treated with zinc dimethyldithiocarbamate (Figure 2). Four experiments, represented by different symbols, were run with concentrations ranging from 0.01 to 0.05%. The breakdown curves resulted in a graded series of intercepts of the 50% ordinate corresponding to increasing dosages. From these a dosage–response relationship was established which included the 10-day intercept at about 0.035%.

A number of other fungicides were studied in like manner, and similar dosage–response relationships were found. The ED_{50} values obtained for these preparations are listed in Table III[2] in order of decreasing effectiveness based on the active ingredient in the solution. With the exception of copper oleate and 8-hydroxyquinoline, which should perhaps be considered as controls representing respectively a poor fungicide and a compound having good inhibitor properties in pure culture tests but poor fungicidal properties, the values range from 0.01% for phenylmercuric acetate to 0.7% for the quaternary ammonium salt.

Several of the more active fungicides were then tested in mixtures in which each compound was tested singly and in factorial combinations with the other. Several concentrations of each compound having ED_{50} values close to the 10 day level were used. It was thought that if the compounds interacted synergistically, the soil life would be greatly extended over that to be expected from the experience with single compounds.

The results obtained with zinc dimethyldithiocarbamate and 2-mercaptobenzothiazole and with mixtures of the two are shown in Table IV. The soil life with the compounds used singly agreed closely

[2] Thanks are due to the following companies for supplying samples used in this study: E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.; Gallowhur Chemical Corp., New York, N. Y.; Geigy Chemical Corp., Ardsley, N. Y.; Hercules Powder Co., Wilmington, Del.; Monsanto Industrial Chemicals, St. Louis, Mo.; Nuodex Products Co., Elizabeth, N. J.; Rohm and Haas Co., Philadelphia, Pa.; Sindar Corp., New York, N. Y.; and R. T. Vanderbilt Co., New York, N. Y.

with the values reported in Table III. When used in combination, the results indicated simple additive effects with no evidence of synergism. However, at the lower concentrations, there was indication of antagonism.

Other experiments were run using combinations of phenylmercuric acetate plus zinc dimethyldithiocarbamate or 2-mercaptobenzothiazole, and zinc dimethyldithiocarbamate plus copper *n*-nitroso-*n*-phenyl hydroxylamine. In none of these was there any suggestion of synergistic action.

Discussion

The concentrations of fungicides prescribed for the protection of fabrics and other materials against the ravages of fungi are usually as high as possible consistent with such factors as cost, ease of application, and toxicity. Hence, most of the information in the literature deals with results of the prolonged exposures needed to cause breakdown of fabrics treated with concentrations used in actual practice. Very little information is available on the minimum concentrations needed to provide a threshold protection in the soil burial test.

In the comparison of fungicides, short-term experiments with minimal concentrations have several advantages over longer experiments with higher concentrations. In addition to the obvious saving of time and materials, short-term tests are less subject to variation between replicates. The smooth deterioration curves of untreated and minimally treated fabrics (Figures 1 and 2) are evidence of a biological uniformity which compares favorably with other laboratory test methods in general use. It should be noted that these smooth curves were obtained with only 3 replicate strips in contrast to the 10 or more replicates required in long-term tests.

After very long incubations one strip of a set frequently breaks down much sooner than its replicates. This variation in breaking strength after long periods of soil burial has been a cause of great concern to workers in this field [2]. It is frequently concluded that the variability in tensile strength is the result of nonuniformity of application of the fungicide, but other alternatives must be considered.

The discoloration due to fungal growth is very even and regular on untreated strips and all treated strips having a short soil life. This was observed not only within experiments but also between experiments. Strips that were treated with higher concentrations of fungicide and incubated longer exhibited localized fungal growth at one spot with most of the strip remaining unattacked. These spots may have arisen from a peculiarity in the adjacent soil or a weak point in the fabric. Once established these spots spread rapidly into adjacent areas of the fabric, perhaps by the production of metabolic acid or adaptive enzymes. Longer incubations increase the probability of localized spotting and the attendant variability in breaking strength.

Also, with higher concentrations and longer incubations there is greater opportunity for the fungicides to react and dissociate variably under the influence of nonbiological effects such as leaching, hydrolysis, or oxidation. The more such factors come into play

TABLE III. Concentrations of Fungicide Treating Solution Yielding ED_{50} Values at 10 Days Soil Burial

Active ingredient	Concentration
Phenylmercuric acetate	0.01%
Zinc salt of dimethyldithiocarbamate and 2-mercaptobenzothiazole	0.025%
Zinc dimethyldithiocarbamate	0.035%
4,5-Dichlorobenzoxazolinone	0.05%
Copper 8-quinolinolate	0.05%
2-Mercaptobenzothiazole	0.1%
Copper naphthenate	0.25%
Copper *n*-nitroso-*n*-phenyl-hydroxylamine	0.25%
2,2'-Methylenebis(4-chlorophenol)	0.3%
Salicylanilide	0.5%
Trimethylcetyl ammonium pentachlorophenate	0.6%
Dehydroabietylamine	0.6%
Dodecyldimethylbenzylammonium cyclopentane carboxylate salt	0.7%
Copper oleate	1.5%
8-Hydroxyquinoline	4–5%

TABLE IV. Effects of Mixtures of Compounds on Fabrics in Soil Burial Tests

Concentration of zinc dimethyldithiocarbamate solution	Days to 50% loss: Concentration of 2-mercaptobenzothiazole solution 0	0.1%	0.2%
0	3	10	12
0.02%	8	11	19
0.04%	11	20	21

the less reliable is the soil burial test as a measure of antifungal activity.

The results with the combination of zinc salts of dimethyldithiocarbamate and 2-mercaptobenzothiazole (Table III) which has been patented [3] as a synergistic mixture do indeed indicate that this mixture has greater activity on fabrics than the compounds used singly. However, laboratory prepared mixtures of these did not indicate synergism as tested by this method (Table IV). These compounds tested in pure culture spore germination in shaker flasks [1] did show synergism with certain concentrations but antagonism with others. Further study of these effects is needed.

With the concentrations used in these studies, it was found that a log–log plot of days to 50% loss vs concentration yields a straight line relationship up to at least 50 days burial. With phenylmercuric acetate, the compound most extensively studied here, this covered a concentration range from 0.002% to 0.5%. The course of the curve beyond these limits is now being studied in these laboratories.

It is interesting to note that the fungicides in wide use today all have ED_{50} values in this test not higher than 0.5%. This level might be considered an end point in accepting or rejecting a candidate fungicide for further testing.

Data about minimal concentrations have value in the study of the kinetics of deterioration. The slopes of the curves of a graded series of concentrations are parallel, and these indicate a corresponding graded series of inflection points where breakdown is first noticed. Once breakdown starts, it proceeds at about the same rate no matter what the initial concentration may have been. Thus, the soil burial life can be broken down into two phases, the first in which no loss in strength is noted, the second in which the fabric is rapidly destroyed. Knowledge of this threshold in the breakdown curve coupled with understanding of the processes which are responsible for reducing the fungicide level from the initial to the threshold, or at least knowledge of the rate at which a fungicide disappears from the fabric, can furnish a basis for treating a fabric with a concentration designed to give any predetermined life in the soil. Various aspects of this problem are being actively studied by one of us (A. G. K.) and will be reported elsewhere.

Summary

A series of commercial fungicides was evaluated for effectiveness in protecting cotton duck in a laboratory soil burial test. Minimal concentrations were applied to give a half-life (50% loss in breaking strength) of 10 days, defined as ED_{50}. Fourteen preparations had ED_{50} values between 0.01% and 1.5% based on the nominal concentration of the treating solution. The more widely used materials all had ED_{50} values not greater than 0.5%.

Acknowledgment

Thanks are due Mr. Marvin Greenberger for chemical analyses and to Mr. Bruce MacDonald for assistance in the preparation of strips.

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Manuscript received November 15, 1961.